(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 896 793 A1

(12) # EUROPEAN PATENT APPLICATION

(43) Date of publication:
17.02.1999 Bulletin 1999/07

(51) Int Cl.6: A22C 13/00

(21) Application number: 98306157.3

(22) Date of filing: 31.07.1998

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 12.08.1997 US 909943

(71) Applicant: VISKASE CORPORATION
Chicago, Illinois 60638 (US)

(72) Inventor: Ducharme, Paul Edmund, Jr.
Tinley Park, Illinois 60477 (US)

(74) Representative: W.P. THOMPSON & CO.
Eastcheap House
Central Approach
Letchworth, Hertfordshire SG6 3DS (GB)

(54) ## Method of making a cellulose food casing including solvent recovery

(57) Disclosed is a method of extruding a solution of cellulose and an amine oxide cellulose solvent as a tube 44 about a sizing mandrel 46 which diametrically stretches the extruded tube. An aqueous PEO solution is introduced into the interior of the extruded tube to facilitate passage of the tube over the sizing mandrel and to extract the amine oxide cellulose solvent from the tube. The extruded tube 24 passes into a regenerating bath 22 containing an aqueous solution of amine oxide solvent. The tube 24 is then transported through a series of wash tubs 36, plasticised by contact with glycerine 30 and dried. Amine-rich portions of the regenerating bath 22 and from the wash tubs 26 are mixed in a line 36 with liquid from the interior of the tube 44. The aqueous PEO solution in line 36 containing the extracted amine oxide cellulose solvent is contacted with an anion exchanger 38, to remove the PEO, a cation exchanger 40 and a heat exchanger 42, so the amine oxide cellulose solvent can be recovered and fed back into the system.

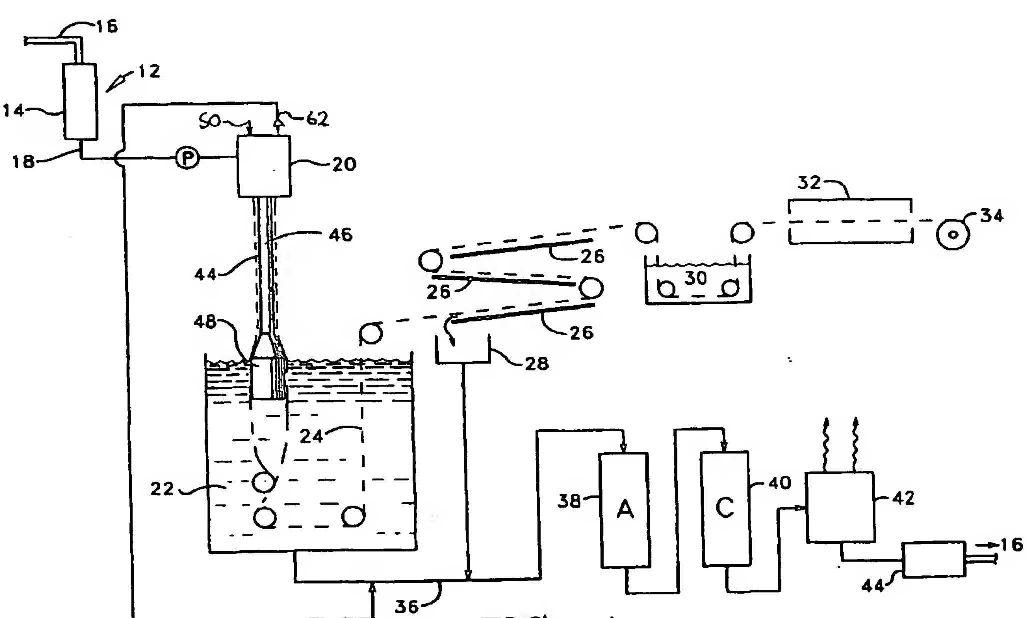


FIG. 1

EP 0 896 793 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a method of forming a cellulose tube, suitable for use as a food casing, using a solution of nonderivatized cellulose, a tertiary amine oxide cellulose solvent and water.

BACKGROUND OF THE INVENTION

[0002] The manufacture of seamless cellulose tubes for sausage casings using cellulose derived by the so-called "viscose process" is well known in the art. Briefly, in the viscose process, a natural cellulose such as cotton linters or wood pulp is reacted chemically to form a cellulose derivative (cellulose xanthate) which is soluble in a weak caustic solution. The solution or "viscose" is extruded as a tube into an acid bath. The extruded viscose reacts chemically with the acid bath resulting in the regeneration and coagulation of a pure cellulose tube. The chemical reaction produces several by-products including hydrogen sulfide and carbon disulfide.

[0003] More recently, a process of direct cellulose dissolution has been adapted to the manufacture of cellulose food casings. In this process no cellulose derivative is formed so the chemical reactions required first to form a cellulose derivative and then to regenerate the cellulose from the derivative have been eliminated. Instead, a natural cellulose is put directly into solution with the use of a tertiary amine oxide cellulose solvent such as N-methyl-morpholine-N-oxide (NMMO). The resulting solution is thermoplastic in that it hardens upon cooling and flows on reheating. The solution, when molten, can be extruded into a water bath. The NMMO solvent is extracted in the water bath so that a regeneration of the cellulose solution occurs. Use of NMMO as a solvent for cellulose eliminates the need for derivatizing the cellulose, as in the viscose process. This avoids certain disadvantages of the viscose process such as the generation of gaseous sulfur compounds during the regeneration process.

[0004] U.S. Patent Nos. 2,179,181; 4,145,532; 4,426,228 and Canadian Patent No. 1,171,615 all deal with the formation of a cellulose solution using the NMMO solvent and subsequent formation of cellulose articles such as films and filaments using the resulting solution. An apparatus and method for preparing an extrudable cellulose solution in a continuous process are disclosed in U.S. Patent Nos. 5,094,690 and 5,330,567. In these patents, a suspension of cellulose in an aqueous solution of NMMO is fed into the top of a vessel having a heated wall. Within the vessel, a rotating wiper spreads the suspension across the heated wall and moves the suspension downward in the vessel. As the suspension moves downward, water is evaporated and the concentration of NMMO increases. Eventually, the temperature of the suspension and the concentration of NMMO reaches a level where the cellulose is dissolved so that a cellulose solution flows from the bottom of the vessel.

[0005] U.S. Patent Nos. 5,277,857; 5,451,364 and 5,597,587 disclose a tubular extrusion method and apparatus utilizing the thermoplastic cellulose solution for purposes of making tubular films. Such films, for example, may be used as sausage casings.

[0006] As disclosed in these patents, the cellulose solution is extruded through an annular die and into a bath of nonsolvent liquid. This can be, for example, water but a nonsolvent concentration of water and NMMO is preferred. This is because one advantage of this direct cellulose dissolution method for producing a cellulose film is that the solvent is recoverable and can be reused. This adds to the economy of the method in that the solvent extracted during cellulose regeneration can be recycled into the system to dissolve the natural cellulose for extrusion. Thus, while water alone is preferred from the standpoint of the speed of cellulose regeneration, an initial higher concentration of NMMO in the bath renders the recovery of the solvent for reuse more cost effective. For example, a regenerating bath having an initial concentration of at least 10 wt% NMMO is considered cost effective for solvent recovery with a range of 15 to 50 wt% being preferred.

[0007] A method for recovering the NMMO is disclosed in WO 93/11287. Briefly the method involves a step of purifying the bath liquid (water + NMMO) by treatment with a strongly basic anion-exchange resin wherein the resin is regenerated by successive treatments with an aqueous solution of a strong inorganic acid and an aqueous solution of sodium hydroxide.

[0008] For purposes of forming tubular films as disclosed in the above referenced patents, the extrusion occurs about a mandrel which depends from the die. An accommodation is made for the introduction of liquid from the regenerating bath into the volume inside the extruded tube. This introduction of the regenerating liquid into the interior of the extruded tube is said to perform several functions. These include, for example, lubrication of the mandrel to facilitate passage of the extruded tube and initiation of the regeneration of cellulose at the inner surface of the extruded tube.

[0009] For purposes of size control of the extruded tube, it is preferred that the mandrel have a section which is larger in diameter than the extruded tube so that the tube is diametrically expanded as it passes over the mandrel. However it has been found that when the mandrel diameter is larger than the extruded tube diameter, water alone is not a sufficient lubricant.

[0010] Introducing a lubricant such as an oil or the like into the interior of the extruded tube was not attempted because this would add a third component (the lubricant) which would complicate the recovery of the NMMO. Accordingly, a solution of water and NMMO has been preferred for introduction into the extruded tube. The solution for such introduction can be drawn directly

from the regenerating bath (the "outer bath") and introduced into the extruded tube through the mandrel as disclosed, for example, in U.S. Patent No. 5,277,857. To insure that the extruded tube does not bind on the mandrel, a higher minimum concentration of 30 wt% NMMO solvent is useful with a preferred range being 30 to 50 wt% as disclosed in U.S. Patent No. 5,451,364. Thus, an operable system can use a 15 wt% NMMO concentration for the outer bath liquid and a 30 wt% NMMO concentration for the liquid introduced into the extruded tube. In subsequent stages of the manufacturing operation these liquids become mixed for extraction and reuse of the solvent.

[0011] For process purposes, it is desirable to regenerate the cellulose from the extruded tube as quickly as possible. For example, it is known that a rapid regeneration produces a more dense cellulose structure which in turn enhances the strength of the cellulose film which is produced. This desire for rapid regeneration is offset by the need for introducing more lubricant into the interior of the extruded tube and the desire for efficient solvent recovery. Accordingly, as noted above, an NMMO solution has been used for both liquids instead of water alone. It now has been discovered that the solvent can be eliminated entirely from the liquid introduced into the interior of the extruded tube without sacrificing lubricating properties to prevent binding of the extruded tube to the mandrel. The elimination of solvent has the added advantage that the regeneration of cellulose at the inner surface of the extruded tube is accelerated resulting in a denser cellulose structure and enhanced properties.

[0012] It has been found that the addition of a suitable surfactant, preferably a nonionic poly(ethylene oxide) rather than NMMO or other lubricant, will provide sufficient lubricity to prevent binding of the extruded tube to the mandrel. Thus, the surfactant addition eliminates the need for having NMMO solvent in the liquid introduced into the interior of the extruded tube (thereby providing the advantage of speeding regeneration) while providing the necessary lubrication to prevent binding.

[0013] The liquid introduced into the interior of the extruded tube eventually is drawn into a volume within the extruded tube below the mandrel. This volume or "inner bath" along with water and surfactant, contains an amount of NMMO solvent extracted from the extruded tube. Liquid removed from the inner bath as disclosed in U.S. Patent No. 5,277,857 can be mixed with liquid from the outer bath for solvent recovery. The presence of the surfactant in the mixture of the inner and outer baths was found not to interfere with solvent recovery. This is because the bath mixture, prior to solvent recovery, is subjected to an anion exchange column. The anion column which is designed to remove certain by-products of cellulose dissolution and regeneration also removes the nonionic poly(ethylene oxide) surfactant which then is destroyed during the acid regeneration of the column. Thus, it has been found that the use of a nonionic poly(ethylene oxide) surfactant does not introduce a third component that complicates recovery of solvent from the bath.

SUMMARY OF THE INVENTION

[0014] In accordance with the present invention, the starting material is a cellulose solution comprising a natural cellulose which has been subject to a direct dissolution by a solvent comprising an aqueous solution of an amine oxide. Processes for such dissolution using an aqueous solution of N-methylmorpholine-N-oxide (NMMO) are known in the art and form no part of the present invention. The product of such a dissolution process is an extrudable solution typically having a melting temperature of about 60 to about 70°C which is extrudable at a temperature of about 70 to about 105°C and comprising 10 to 20 wt% cellulose, 70 to 80 wt% NMMO and 5 to 15 wt% water.

[0015] The cellulose solution is characterized hereafter as being a nonderivatized cellulose solution. For purposes of this specification, the term "nonderivatized" cellulose means a cellulose which has not been subjected to covalent bonding with a solvent or reagent but which has been dissolved by association with a solvent or reagent through for example Van der Waals forces such as hydrogen bonding.

[0016] The cellulose solution is extruded through an annular die and about a mandrel which depends from the die. Suitable extrusion methods and apparatus for such extrusion are disclosed in U.S. Patent Nos. 5,277,857; 5,451,364; 5,766,540 and 5,759,478, the disclosures of which are incorporated herein by reference.

[0017] In the above referenced patents, extrusion from the die is downward through an air gap and into an outer bath of nonsolvent liquid. "Nonsolvent" as used herein means a liquid which is not a cellulose solvent and preferably is water or a nonsolvent concentration of NMMO in water. In the outer bath, the NMMO is extracted from the extruded tube through the tube outer surface thereby coagulating and regenerating the nonderivatized cellulose to form a tube composed of a cellulose gel. The gel tube is washed to remove residual NMMO solvent. Then it is plasticized with a polyol such as glycerine and dried to form a tubular film.

[0018] For purposes of size control, the cellulose solution is extruded in the present invention about a mandrel which diametrically stretches the extruded tube prior to entering the outer bath. The mandrel also is structured to accommodate the introduction of a nonsolvent liquid into the interior of the extruded tube. Non-solvent liquid introduced into the interior of the extruded tube has the functions of at least the initiation of solvent extraction from the inner surface of the extruded tube and lubrication of the mandrel to prevent the extruded tube from binding to the mandrel surface.

[0019] As noted above, water alone is in principle preferred for rapid solvent extraction. However, in some sit-

uations, water alone is not a suitable mandrel lubricant. One situation where this is the case where the mandrel diameter is larger relative to the extruded tube diameter for purposes of diametrically sizing the extruded tube. In this case, NMMO has in the past been added to the water introduced into the interior of the extruded tube to provide the necessary slip to prevent binding of the extruded tube to the mandrel surface.

[0020] For purposes of economy, the NMMO extracted from the extruded tube is desirably recovered for reuse in the dissolution process. For this purpose the regenerating liquids coming in contact with both the inner and outer surfaces of the extruded tube have been removed, mixed together and processed to extract the NMMO. It should be appreciated that the presence of a third liquid component (other than water and NMMO) would be expected to complicate recovery of the NMMO. It is for this reason that the nonsolvent introduced into the interior of the extruded tube has in the past contained NMMO to provide the required "slip" rather than another lubricant such as an oil even though use of NMMO compromises the rate of solvent extraction from the inner surface of the extruded tube.

[0021] It now has been found that adding a suitable surfactant such as poly(ethylene oxide) to the nonsolvent introduced into the interior of the extruded tube (preferably to the exclusion of NMMO) will provide the required mandrel lubrication without compromising the NMMO extraction characteristics of water alone and without interfering with the subsequent recovery of the NMMO.

[0022] A suitable surfactant for purposes of the present invention is one which is removable from the bath liquid by the action of an anion exchange resin, conveniently a strongly basic anion-exchange resin as may be used for purifying the NMMO. A preferred surfactant is a nonionic poly(ethylene oxide) referred to herein as PEO. PEO is an olefinic oxide polymer having a molecular weight of at least about 70,000 and up to about 5,000,000. It is a free-flowing powder which is soluble in water at temperatures up to 98°C. PEO is commercially available from Union Carbide Corporation under the trademark POLYOX®. POLYOX water soluble resins, CAVES Registry NO. 25 322-68-3 are described as being nonionic water soluble polymers of PEO which are available in a range of molecular weights.

[0023] It has been found that the PEO does not compromise the ability of the nonsolvent liquid to extract NMMO from the extruded tube and it provides sufficient lubrication to prevent the extruded tube from binding to the mandrel surface. More important, the PEO does not present problems during the recovery of the NMMO because it is removed by the anionic exchange resin, preferably the strongly basic anion-exchange resin used in the purification of the NMMO. Thereafter, the PEO removed by the resin may be destroyed and washed from the resin during the regeneration of the resin with an inorganic acid such as HCl.

[0024] Accordingly, the present invention is characterized by a method of forming a tubular film by tubular extrusion of a nonderivatized cellulose solution comprising cellulose, NMMO cellulose solvent and water including the steps of introducing into the extruded tube interior, a nonsolvent liquid which is preferably free of NMMO cellulose solvent and which comprises water and a suitable surfactant to extract NMMO solvent from the inner surface of the extruded tube. The nonsolvent then is removed for recovery of the NMMO solvent, the recovery process including contact by an anion exchange resin which removes the surfactant thereby leaving a solution of NMMO and water from which the NMMO is removed for reuse.

[0025] In particular the present invention provides in one aspect a process for forming a tubular cellulose tube comprising the steps of:

a) forming a thermoplastic solution comprising a nonderivatized cellulose, NMMO and water;
b) extruding the solution through an extrusion die having an annular extrusion orifice to form an extruded tube of the solution;
c) passing the extruded tube over and about a mandrel which depends from the die, the mandrel having a portion which defines a cylindrical surface which is larger in diameter than the extruded tube for contacting and diametrically expanding the extruded tube and thereafter passing the extruded tube into an outer bath comprising a nonsolvent liquid, preferably water and a concentration of 10 to 30 wt% NMMO;
d) contacting the extruded tube with the outer bath for regenerating the cellulose and forming a hydrated cellulose tube by extracting the NMMO from the extruded tube;
e) introducing a nonsolvent liquid comprising water and PEO into the interior of the extruded tube, to form a pool within the extruded tube and about the mandrel cylindrical surface, the pool contacting the extruded tube inner surface for initiating the extraction of NMMO from the inner surface of the extruded tube so as to commence the regeneration of cellulose at said inner surface;
f) removing the nonsolvent liquid and extracted NMMO from the pool by drawing between the extruded tube inner surface and the mandrel cylindrical surface and into an inner bath contained inside the hydrated cellulose tube and below the mandrel;
g) said drawing of nonsolvent liquid from the pool providing lubrication of the mandrel cylindrical surface to facilitate passage of the extruded tube over the mandrel cylindrical surface;
h) removing and combining portions of the inner and outer baths to form a mixture comprising water, NMMO extracted from the extruded tube and PEO;
i) contacting the mixture with an anion exchange resin so as to provide a PEO-free solution of water

and NMMO; and

j) separating water from the PEO-free solution to provide a higher NMMO concentration and using the higher NMMO concentration in the formation of the thermoplastic solution for the extrusion at step (a).

[0026] Accordingly, it is an advantage of the present invention that it can provide a process for regenerating a seamless cellulose tube (suitable for use as a sausage casing) from a solution of nonderivatized cellulose, a tertiary amine oxide cellulose solvent and water in which regeneration of the cellulose at the inner surface of the extruded tube is accelerated.

[0027] Another advantage is that, in at least some processes according to the invention, the regeneration of cellulose at the inner tube surface is accelerated by introducing a solvent-free regenerating liquid into the interior of the extruded tube.

[0028] A further advantage is that extrusion occurs about a mandrel which diametrically expands the extruded tube and the regenerating liquid, which may be solvent-free, introduced into the interior of the extruded tube is an aqueous solution containing a lubricant to prevent the binding of the extruded tube to the mandrel.

[0029] Yet another advantage is that the lubricant which is a component of the regenerating solution does not interfere with the subsequent purification and recovery of NMMO from the regenerating liquids.

DESCRIPTION OF THE DRAWINGS

[0030] The invention will now be described by way of example with reference to the drawings, in which:

Figure 1 is a view showing in schematic fashion steps of a process for extruding tubular films and solvent recovery; and

Figure 2 is a view showing a portion of the tubular extrusion apparatus shown in Figure 1.

DETAILED DESCRIPTION OF THE INVENTION

[0031] Referring to the drawings, Figure 1 shows a schematic representation of a tubular extrusion system for the production of tubular films of the type as may be used for sausage casings or the like. Briefly, the system includes apparatus generally indicated at 12 for solubilizing a natural cellulose. For example the apparatus can be the type as described in U.S. Patents 5,094,690 and 5,330,567 as referred to hereinabove. In this apparatus, a mixture of natural cellulose, water and an amine oxide cellulose solvent such as NMMO is introduced into the top of a heated vessel 14 through an inlet 16. As the mixture moves to the bottom of vessel 14, water is evaporated and a cellulose solution, hereafter referred to as "dope", is forced from a bottom outlet 18. The dope is pumped to an extrusion die 20 arranged for extruding a seamless tube 44 of the dope downwardly into a regenerating bath 22. The regenerating bath 22 contains a nonsolvent liquid. An aqueous solution of 5 to 30 wt% NMMO is preferred. In the bath, the amine solvent is extracted from the extruded tube so as to coagulate and regenerate the cellulose from the solution to form a seamless tube 24 of a hydrated cellulose gel. Accordingly, the NMMO concentration in the bath is enriched as NMMO is extracted from the extruded tube.

[0032] The hydrated cellulose tube 24 is transported through a series of wash tubs 26 to remove residual amounts of the amine solvent. The flow through the wash tubs 26 is countercurrent and the amine rich wash water is collected by a drain 28. After washing, the tube is placticized by contact with a glycerine solution 30 and then is dried by passing through a drier 32 to form the cellulose tubular film which is gathered onto a reel 34.

[0033] For purposes of economy, amine rich portions of the regenerating bath 22 and wash water from drain 28 are collected and mixed together as in a flow line 36. This mixture is fed through successive anion and cation exchangers 38, 40 respectively to remove ions which may have been generated during the dope making, extrusion and cellulose regenerating processes. The purified mixture then is fed to a heat exchanger 42 to evaporate water and concentrate the amine oxide cellulose solvent (NMMO). The recovered concentrated cellulose solvent then is fed back to the system for purposes of solubilizing the cellulose and making the dope to be extruded. For example, the recovered solvent can be fed to a mixer 44 where it is mixed with a natural cellulose pulp and water to form a suspension which is fed through inlet 16 to the vessel 14.

[0034] As part of the extrusion process, the extruded tube 44 of the cellulose solution is passed over a mandrel 46 which depends from the extrusion die. A lower portion 48 of the mandrel has a diameter larger than the extruded diameter of the dope tube. Accordingly, the extruded tube is diametrically expanded as it passes over the cylindrical surface defined by the diameter of the mandrel lower portion 48. As disclosed in U.S. Patent Nos. 5,277,857 and 5,451,364, it is preferred to introduce a nonsolvent into the extruded tube to initiate the regeneration of the cellulose at the inner surface of the extruded tube and provide the necessary lubrication to prevent binding of the extruded tube to the mandrel. In this example of the present invention, the nonsolvent so introduced comprises a mixture of poly(ethylene oxide) and water.

[0035] Reference is made to U.S. Patent Nos. 5,277,857 and 5,766,540 for a detailed description regarding the apparatus and method for introducing nonsolvent into the extruded tube. Briefly, and as shown in Figure 2, the mandrel 46 is provided with internal inlet and outlet conduits 50 and 62 respectively.

[0036] Inlet conduit 50 communicates with an outlet 52 just above the enlarged lower portion 48. Nonsolvent which is introduced through the mandrel forms a pool

ing water and PEO for:

(a) extracting NMMO solvent from the inner surface of the extruder wherein the extracted NMMO mixes with the nonsolvent liquid and
(b) lubricating the interface between the mandrel and the extruded tube for facilitating the passage of the extruded tube over the mandrel portion of larger diameter.

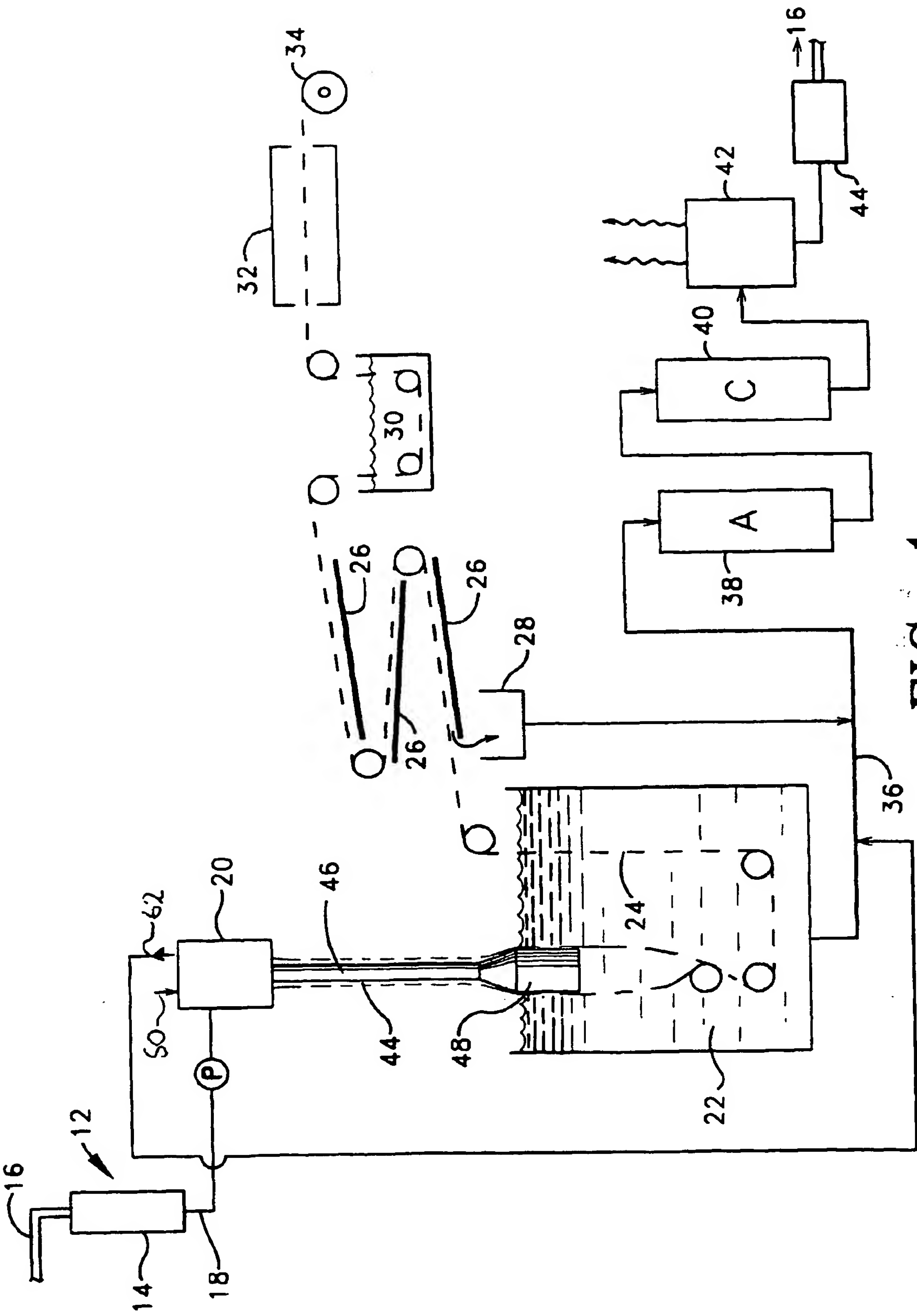
13. A method according to claim 12, including the steps of:

(a) recovering at least part of the mixture of nonsolvent liquid and extracted NMMO;
(b) passing the mixture through an anion exchanger for removing the PEO in the mixture to form a PEO-free NMMO aqueous solution;
(c) separating water from the PEO-free NMMO aqueous solution to form a concentrated NMMO aqueous solution; and
(d) employing the concentrated NMMO aqueous solution to form the extrudable solution of nonderivatized cellulose, NMMO cellulose solvent and water.

14. A method according to any of claims 1 to 6, 12 and 13, wherein the nonsolvent liquid introduced into the interior of the extruded tube is essentially free of NMMO.

15. A method according to claim 14, wherein the nonsolvent liquid consists essentially of water and PEO.

16. A method according to any of claims 1 to 6 and 12 to 15, wherein the nonsolvent liquid introduced into the interior of the tube contains about 0.01 wt% of PEO.



16
14
18
12
P
50
62
20
44
46
48
22
24
26
26
26
26
28
30
32
34
36
38
A
40
C
42
44
16

FIG. 1

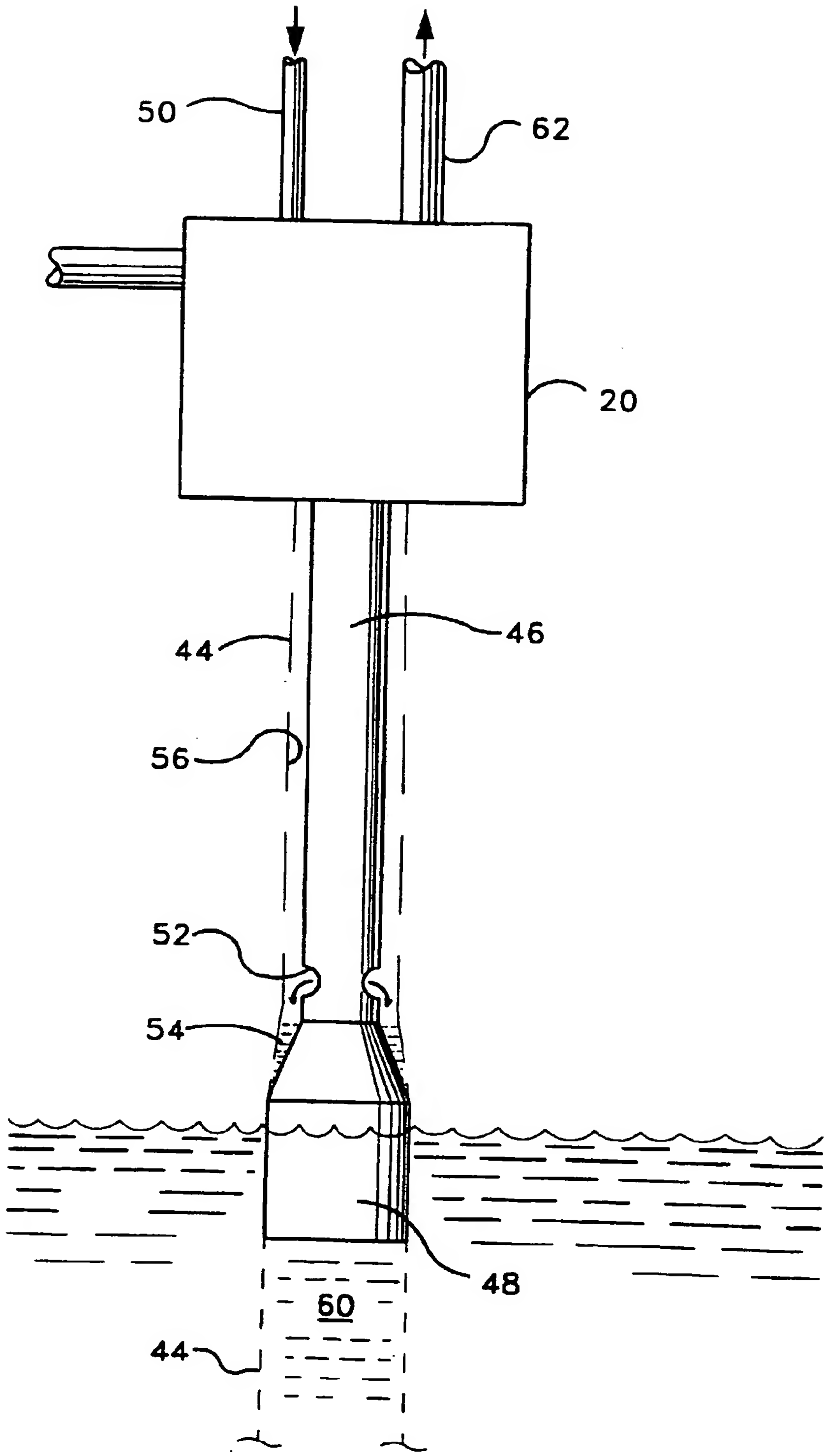


FIG. 2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 6157

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	WO 93 13670 A (VISKASE CORPORATION) 22 July 1993 * page 21, paragraph 2; claims 1-38; figures 1,2 *	1	A22C13/00
D,A	WO 93 11287 A (COURTAULDS PLC) 10 June 1993 * claims 1-18 *	1	
D,A	US 4 145 532 A (N. E. FRANKS) 20 March 1979 * claims 1-10 *	1	
A	FR 2 464 651 A (VISCOFAN, INDUSTRIA NAVARRA DE ENVOLTURAS CELULOSICAS, SA) 20 March 1981 * claims 1-4 *	1	
A	EP 0 756 825 A (VISKASE CORPORATION) 5 February 1997 * page 5, line 9 - page 7, line 32; claims 1-17; figures 1,2 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	DE 44 21 482 A (FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG E. V.) 21 December 1995 * claims 1-15 *	1	A22C C08J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 November 1998	Permentier, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document